



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08G 69/48, 69/08, 69/16	A1	(11) International Publication Number: WO 00/35992 (43) International Publication Date: 22 June 2000 (22.06.00)
---	----	--

(21) International Application Number: PCT/NL99/00764

(22) International Filing Date: 13 December 1999 (13.12.99)

(30) Priority Data:
1010819 16 December 1998 (16.12.98) NL(71) Applicant (for all designated States except US): DSM N.V.
[NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): NIJENHUIS, Atze, Jan
[NL/NL]; Gangeltstraat 2, NL-6132 HB Sittard (NL).
ABERSON, René [NL/NL]; Balladelaan 25, NL-3813 CA
Amersfoort (NL). SCHOLTENS, Boudewijn, Jan, Robert
[NL/NL]; Gelrestraat 12, NL-6151 JA Sittard (NL).(74) Agent: VAN BORM, Werner, August, Hendrik, Maria; DSM
Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen
(NL).(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG,
BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE,
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,
MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU,
SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG,
US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE,
LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT,
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.

(54) Title: INTRINSICALLY GEL-FREE, RANDOMLY BRANCHED POLYAMIDE

(57) Abstract

The invention relates to a randomly branched polyamide comprising at least units derived from: 1. AB monomers; 2. at least one compound I, being a carboxylic acid (A_v) having a functionality $v \geq 2$ or an amine (B_w) having a functionality $w \geq 2$; 3. at least one compound II, being a carboxylic acid (A_v) having a functionality $v \geq 3$ or an amine (B_w) having a functionality $w \geq 3$, compound II being a carboxylic acid if compound I is an amine or compound II being an amine if compound I is a carboxylic acid and the amounts of all units derived from carboxylic acids and amines in the polyamide satisfying conditions as mentioned in claim 1. The composition of the randomly branched polyamide is such that it cannot form a crosslinked polyamide (and thus no gels, either), in particular during the prepolymerization, the polymerization, the post-condensation, the processing and the storage of the randomly branched polyamide, and this at a variety of ambient factors, for instance at elevated temperature and pressure. The polyamide is eminently suitable for the production of fibre and film, in particular for flat film.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5 INTRINSICALLY GEL-FREE, RANDOMLY BRANCHED POLYAMIDE

The invention relates to a randomly branched polyamide comprising at least units derived from:

- 10 1. AB monomers,
 2. at least one compound I, being a carboxylic acid (A_v)
 having a functionality $v \geq 2$ or an amine (B_w) having
 a functionality $w \geq 2$,
 3. at least one compound II, being a carboxylic acid
15 (A_v) having a functionality $v \geq 3$ or an amine (B_w)
 having a functionality $w \geq 3$, compound II being a
 carboxylic acid if compound I is an amine or
 compound II being an amine if compound I is a
 carboxylic acid.

20 In the context of this application, with
the term "randomly branched" is meant that the
branching points are randomly distributed in the
polyamide chain.

 Such a randomly branched polyamide is known
25 from EP-345.648-B1. However, a problem encountered with
the randomly branched polyamide according to EP-
345.648-B1 is that the randomly branched polyamide is
not intrinsically gel-free so that, while the randomly
branched polyamide can for instance be obtained as a
30 gel-free melt, during further processing of the
randomly branched polyamide, gel formation may as yet
occur. In the context of this application gel formation
is understood to be a process involving the formation
of a network in a polymer material. Gel formation gives
35 rise to, among other things, the formation of visible
inhomogeneities ("gels") during processing of the

randomly branched polyamide into, for instance, films or fibres and to deterioration of the mechanical properties of polyamide objects obtained from the randomly branched polyamide. It is also known that when
5 randomly branched polyamide is processed in equipment where local overheating may take place or where polyamide material may accumulate, for instance in extruders and mixers, it may contain strongly crosslinked polyamide.

10 It is desirable to have intrinsically gel-free randomly branched polyamide available. In the context of this application "intrinsically gel-free" is understood to mean that the composition of the randomly branched polyamide is such that it cannot form
15 crosslinked polyamide (and therefore no gels), in particular during the prepolymerization, the polymerization, the post-condensation, the processing, for instance into films or fibres, and the storage of the randomly branched polyamide, and this at a variety
20 of ambient factors, for instance at elevated temperature and pressure.

Although the prevention of gel formation in polymeric materials has been receiving a great deal of attention in practice, at this point of time neither a
25 structural nor a systematic approach is known to provide an adequate solution to the problem of obtaining intrinsically gel-free, randomly branched polyamide from AB monomers.

30 It is the aim of the inventors to provide such an intrinsically gel-free, randomly branched polyamide comprising at least units derived from:

1. AB monomers,
2. at least one compound I, being a carboxylic acid (A_v)

having a functionality $v \geq 2$ or an amine (B_w) having a functionality $w \geq 2$,

3. at least one compound II, being a carboxylic acid (A_v) having a functionality $v \geq 3$ or an amine (B_w) having a functionality $w \geq 3$, compound II being a carboxylic acid if compound I is an amine or compound II being an amine if compound I is a carboxylic acid.

This aim is achieved when the amounts of all units derived from carboxylic acids and amines in the polyamide satisfy formula 1

$$P < 1 / [(F_A - 1) \cdot (F_B - 1)] \quad (1)$$

where:

$$P = [\sum (n_i \cdot f_i)]_X / [\sum (n_i \cdot f_i)]_Y \quad (2)$$

where $P \leq 1$ and either $X = A$ and $Y = B$, or $X = B$ and $Y = A$, and

$$F_x = \sum (n_i \cdot f_i^2) / \sum (n_i \cdot f_i) \quad (3)$$

for, respectively, all carboxylic acids ($X = A$) and all amines ($X = B$), where f_i is the functionality of either the carboxylic acid ($f_i = v_i$) or amine ($f_i = w_i$), n_i being the number of moles of the carboxylic acid or amine and the summation involving all units derived from carboxylic acids and amines in the polyamide.

In the context of the present invention AB monomer is understood to be a monomer that has both a carboxylic acid group (A) and an amine group (B).

In the context of the present application

compound I and compound II are also understood to be mixtures of several carboxylic acids having the same functionality or mixtures of several amines having the same functionality.

5 In the context of the present application carboxylic acid and amine are understood to be, respectively, a compound which, besides one or more carboxylic acid groups, does not carry any amine groups and the other way round. It therefore follows that
10 units derived from carboxylic acids or amines in the polymer have a chemical composition that differs from that of the units derived from the AB monomers. Carboxylic acid group is in the context of the present application understood to be a group that can form a
15 covalent bond with an amine group, for instance -COOH, -COHal (Hal = halogen), -CO₂R in which R is an alkyl residue with 1 to 20 carbon atoms and -SO₂Hal (Hal = halogen).

 In the context of the present application
20 functionality is understood to be the number of functional groups in the carboxylic acid or the amine that can form a bond with other carboxylic acids, amines or AB monomers to form the randomly branched polyamide according to the invention. A functional
25 group that cannot form this bond, for instance a sterically hindered amine group or an aromatic amine group, is not considered as a functional group in determining the functionality. Likewise, the
functionality is equated to 1 if two functional groups
30 at a compound are both involved in a single bond with a third functional group, for instance two COOH groups that are close together which form an imide bond with an amine, for instance in the compound orthodicarboxybenzene.

Preferably, the functionality v or w of compound I can be chosen from 2, 3, 4, 5 and 6. More preferably, the functionality of compound I is 2. Preferably, the functionality v or w of compound II can be chosen from 3, 4, 5 and 6. More preferably, the functionality of compound II is 3.

Eligible AB monomers are all AB monomers that can be used for the production of polyamides, in particular α,ω -amino acids and/or lactams, for instance caprolactam, laurine lactam and dodecalactam, as well as the corresponding amino acids and aromatic amino acids, for instance p -(aminomethyl)-benzoic acid. Preferably, the lactam is ϵ -caprolactam.

Eligible carboxylic acids (A_v) are preferably difunctional carboxylic acids, for instance adipic acid, dodecane dicarboxylic acid, isophthalic acid and terephthalic acid and trifunctional carboxylic acids, for instance 1,3,5-tris(caproic acid)melamine, trimesic acid and trimeric fatty acids with 50-60 carbon atoms as well as esters and anhydrides of said carboxylic acids. Preferably, the difunctional carboxylic acid is terephthalic acid. Preferably, the trifunctional carboxylic acid is 1,3,5-tris(caproic acid)melamine (TCAM) or trimesic acid.

Eligible amines (B_w) are preferably difunctional amines, for instance diaminobutane, diaminohexane, diaminododecane, cyclic amines, for instance 1,4-diaminocyclohexane, 4,4'-diaminobicyclohexylamine, 1,3- and 1,4-xylylene diamine and trifunctional amines, for instance trisaminononane and bis(hexamethylene triamine). Preferably, the difunctional amine is 1,6-hexamethylene diamine. Preferably, the trifunctional amine is

bis(hexamethylene triamine).

Besides the units derived from compounds I and II according to the invention also other units derived from carboxylic acids and amines may be present, for instance monofunctional carboxylic acids and amines (chain terminators).

Although the aim of the invention according to EP-345.648-B1 is not the aim of the present invention, while said publication does not mention the measures according to the present invention, either, it does mention, besides a number of randomly branched polyamides that do not satisfy the measures according to the present invention, also a number of randomly branched polyamides which coincidentally satisfy the measures according to the invention. These randomly branched polyamides are excluded from the application, more specifically the randomly branched polyamides that are built up of units derived from carboxylic acids (A_v) having a functionality v and amines (B_w) having a functionality w , in the following amounts (in $\mu\text{mol/g}$ of polyamide):

- B_1 (20), B_3 (60) and A_2 (20)
- B_1 (10), B_3 (60) and A_2 (30)
- B_1 (120), B_2 (30) and A_3 (60)
- B_1 (150), B_2 (30) and A_3 (70)
- B_1 (170), B_3 (30), A_2 (60) and A_3 (60)

The intrinsically gel-free, randomly branched polyamide according to the invention can be produced using methods known to one skilled in the art, both via a batch process and via a continuous process. According to a first embodiment all AB monomers,

carboxylic acids and amines are polymerized in amounts according to the invention in a reactor at a suitable temperature and pressure. According to a second embodiment the carboxylic acids and amines are added to
5 a melt of a polyamide comprising units derived from AB monomers.

The gel-free, randomly branched polyamide according to the invention can also contain the customary additives, for instance flame retardants,
10 fillers, release agents, lubricants and colourants.

The intrinsically gel-free, randomly branched polyamide according to the invention is eminently suitable for the production of fibre, film, foams and moulded articles. In particular, the
15 intrinsically gel-free, randomly branched polyamide according to the invention is eminently suitable for the production of thin film, in particular flat film. The inventors have established that no gels could be observed in said thin film obtained with the polyamide
20 according to the invention. Another surprising advantage of the polyamide according to the invention is that no or hardly any neck-in occurs in the production of flat film. Neck-in is the decrease in the ratio of film width to die width during the film
25 forming process. This surprising advantage allows films to be formed in a simple manner without the known attendant measures to prevent neck-in, for instance cooling of the film edges during the film forming process.

30 The invention therefore also relates to a process for the production of film obtained from the polyamide according to the invention, as well as to the film obtained with the polyamide according to the invention.

The invention will now be elucidated on the basis of examples, without however being limited thereto.

5 Examples

Examples I-VIII : Graphical development of the gel-free concentration range

For a number of combinations of carboxylic acids and amines (Table 1), formulas (1)-(3) were developed into a graphical representation for a combination of three carboxylic acids or amines (Figures 1-8), without however limiting the invention to the examples given. In the figures it was shown what amounts (expressed as mole fractions) of units derived from carboxylic acids and amines an intrinsically gel-free, randomly branched polyamide can contain. In the concentration range indicated by small circles the randomly branched polyamide is non-intrinsically gel-free. It is remarkable to note that the intrinsically gel-free nature of a randomly branched polyamide does not depend on the absolute amount of units derived from a carboxylic acid or amine, but only on the relative ratio of the units derived from the carboxylic acids and amines. This also means that the intrinsically gel-free nature of a randomly branched polyamide according to the invention does not depend on the amount of units derived from AB monomers. A third remarkable fact is that in the polyamide according to the invention all units derived from carboxylic acids can be replaced by amines, and the other way round, without this changing the gel-free nature of a polyamide. For instance, the concentration range for the units derived from carboxylic acids A_1 and A_3 and the amine B_2 is the same

as that for units derived from amines B₁ and B₃ and the carboxylic acid A₂ (Figure 1).

Table 1: Combinations of carboxylic acids and amines

Example	Carboxylic acids	Amines	Figure
I	A ₁ , A ₃	B ₂	1
II	A ₁ , A ₃	B ₃	2
III	A ₁ , A ₄	B ₂	3
IV	A ₁ , A ₄	B ₃	4
V	A ₁ , A ₅	B ₂	5
VI	A ₁ , A ₅	B ₃	6
VII	A ₁ , A ₆	B ₂	7
VIII	A ₁ , A ₆	B ₃	8

Preparation of gel-free, randomly branched polyamides

10 Process 1

100 g of ϵ -caprolactam, 1 g of ϵ -aminocaproic acid, 2 g of water and varying amounts of carboxylic acids and amines (see Table 2 for the molar ratios) were mixed in a glass tube at 90°C. The tube was equipped with a reflux cooler and was purged three times with vacuum/nitrogen before use, following which the reaction mixture was heated to 260-270°C in a nitrogen atmosphere and was subsequently kept at this temperature for 11 hours. After cooling, the tube was broken and its contents ground and washed three times in boiling water so as to remove any unreacted caprolactam and low-molecular oligomers and subsequently dried for 24 hours in a vacuum at 80°C. The polymer obtained was white. The washed and dried

polymers were subjected to a number of analyses such as melt viscosity and intrinsic viscosity. The melt viscosity was determined using a Rheometrix 800 plate/plate apparatus as so-called zero viscosity at 230°C, in other words the dynamic melt viscosity at zero shear force. The intrinsic viscosity was determined by means of a three-point measurement (3, 4 and 5 g/l) in 85% formic acid at 25°C. All polymers in Table 1 were prepared in this way.

Process 2

In a 5-litre reactor 3.5 kg of ϵ -caprolactam, 35 g of ϵ -aminocaproic acid, 70 g of water and the varying amounts of additives were combined. The temperature of the reaction mixture was kept at 90°C for 5 hours, after which the mixture was heated to 275°C in about 2 hours and was kept at that temperature for 5 hours. Subsequently, the temperature was lowered to 240°C in 60 minutes and kept at that value for 3.5 hours. Next, the reactor contents were drained in a nitrogen atmosphere at 1 bar overpressure. The polymer thread flowing out the reactor was cooled in ice water and chopped into granules, which were washed with water at 100°C and subsequently dried.

Post-condensation:

The polymer obtained by means of processes 1 and 2 was post-condensed for 10 hours at 190°C in a vacuum and with a nitrogen leak.

Examples IX-XXXII

Process 1 was used to prepare a number of polyamides, the compositions being given in Table 2. In

none of the polyamides was crosslinking observed during or after the polymerization.

Table 2: Intrinsically gel-free polyamide compositions
(amounts in moles).

5

Ex.	A ₁	B ₁	A ₂	B ₂	A ₃	B ₃	AB monomer
IX	1	-	-	0.25	0.25	-	300
X	1	-	-	0.5	0.5	-	300
XI	1	-	-	0.75	0.75	-	300
XII	1	-	-	1	1	-	300
XIII	1	-	-	2	2	-	300
XIV	-	1	0.25	-	-	0.25	300
XV	-	1	0.5	-	-	0.5	300
XVI	-	1	1	-	-	1	300
XVII	-	1	2	-	-	2	300
XVIII	1	1.25	-	0.25	0.25	-	300
XIX	1	1.5	-	0.5	0.5	-	300
XX	1	2	-	1	1	-	300
XXI	1	3	-	2	2	-	300
XXII	1	1.5	-	0.5	0.5	-	300
XXIII	0.5	-	-	-	0.5	-	300
XXIV	0.33	-	-	0.67	1.33	-	300
XXV	0.5	-	-	0.5	1	-	300
XXVI	0.6	-	-	0.4	0.8	-	300
XXVII	0.67	-	-	0.33	0.67	-	300
XXVII	2	-	-	2	1	-	300
I							
XXIX	0.67	-	-	0.67	1	-	300
XXX	0.5	-	-	0.5	1	-	300
XXXI	0.57	-	-	0.29	0.57	-	300
XXXII	1.33	-	-	1.67	1.33	-	300

Explanation of the abbreviations :

A₁ : benzoic acid

B₁ : hexylamine

5 A₂ : adipic acid

B₂ : hexamethylene diamine

A₃ : 1,3,5-tris(caproic acid)melamine

B₃ : bis(hexamethylene)triamine

AB monomer : ϵ -caprolactam

10

Comparative examples A-G according to EP-B1-345.638

Process 1 was used to prepare a number of polyamides, their compositions being given in Table 3.

15 In all polyamides crosslinking was observed during or after the polymerization.

Table 3 : Comparative examples according to EP-B1-345.638.

Comparative example	Example acc. to EP- B1-345.638 (Table 2)	AB monomer	B ₁ (L-252)	B ₃ (N-TEA)	A ₂ (ADS)	A ₃ (TMS)	gel for- mation
A	10	aminolaurine acid	180	30	-	90	yes
B	11	aminolaurine acid	190	30	-	92	yes
C	13	aminolaurine acid	176	28	46	56	yes
D	15	caprolactam	210	30	-	100	yes
E	16	caprolactam	210	30	-	100	yes
F	17	caprolactam	176	28	46	56	yes
G	18	caprolactam	124	20	32	40	yes

Explanation of the abbreviations:

L-252 : 3-amino-1-cyclohexyl-aminopropane
N-TEA : nitrilotriethane amine
ADS : adipic acid
5 TMS : trimesic acid

Mechanical properties of the polyamide according to the invention

10 Surprisingly, it was also found that the polyamide according to the invention combines a high melt strength with a high melt drawing degree compared to non-branched polyamide. This is shown in Figure 9.

CLAIMS

1. Intrinsically gel-free, randomly branched polyamide comprising at least units derived from:

1. AB monomers,
2. at least one compound I, being a carboxylic acid (A_v) having a functionality $v \geq 2$ or an amine (B_w) having a functionality $w \geq 2$,
3. at least one compound II, being a carboxylic acid (A_v) having a functionality $v \geq 3$ or an amine (B_w) having a functionality $w \geq 3$, compound II being a carboxylic acid if compound I is an amine or compound II being an amine if compound I is a carboxylic acid, characterized in that the amounts of units derived from all carboxylic acids and amines in the polyamide satisfy formula 1

$$P < 1 / [(F_A - 1) \cdot (F_B - 1)] \quad (1)$$

where:

$$P = [\sum (n_i \cdot f_i)]_X / [\sum (n_i \cdot f_i)]_Y \quad (2)$$

where $P \leq 1$ and either $X = A$ and $Y = B$, or $X = B$ and $Y = A$, and

$$F_X = \sum (n_i \cdot f_i^2) / \sum (n_i \cdot f_i) \quad (3)$$

for, respectively, all carboxylic acids ($X = A$) and all amines ($X = B$), where f_i is the functionality of either the carboxylic acid ($f_i = v_i$) or amine ($f_i = w_i$), n_i being the number of

moles of the carboxylic acid or amine and the summation involving all units derived from carboxylic acids and amines in the polyamide except:

5 randomly branched polyamides comprising units derived from carboxylic acids (A_v) having a functionality v and amines (B_w) having a functionality w , in the following amounts (in $\mu\text{mol/g}$ of polyamide):

- 10 - B_1 (20), B_3 (60) and A_2 (20)
- B_1 (10), B_3 (60) and A_2 (30)
- B_1 (120), B_2 (30) and A_3 (60)
- B_1 (150), B_2 (30) and A_3 (70)
- B_1 (170), B_3 (30), A_2 (60) and A_3 (60).

15 2. Polyamide according to claim 1, characterized in that the functionality of compound I can be chosen from 2, 3, 4, 5 and 6 and the functionality of compound II can be chosen from 3, 4, 5 and 6.

20 3. Polyamide according to either of claims 1-2, characterized in that the functionality of compound I is 2 and the functionality of compound II is 3.

25 4. Polyamide according to claim 3, characterized in that also at least a unit derived from monofunctional carboxylic acid or amine is present.

30 5. Polyamide according to either of claims 3-4, characterized in that compound I is chosen from the group formed by terephthalic acid and 1,6-hexa-methylene diamine.

6. Polyamide according to any one of claims 3-5, characterized in that compound II is chosen from

the group formed by 1,3,5-tris(caproic acid)-melamine, trimesic acid and bis(hexamethylene triamine).

- 5 7. Polyamide according to any one of claims 1-6, characterized in that the AB monomer is an α,ω -amino acid and/or a lactam.
8. Polyamide according to claim 7, characterized in that the lactam is ϵ -caprolactam.
- 10 9. Process for the preparation of a polyamide film, characterized in that a polyamide according to any one of claims 1-8 is chosen as polyamide.
10. Fibre, film, foam or moulded article obtained from a polyamide according to any one of claims 1-8.
- 15 11. Flat film obtained from a polyamide according to any one of claims 1-8.
12. Polyamide as described and elucidated on the basis of the examples.

FIG. 1

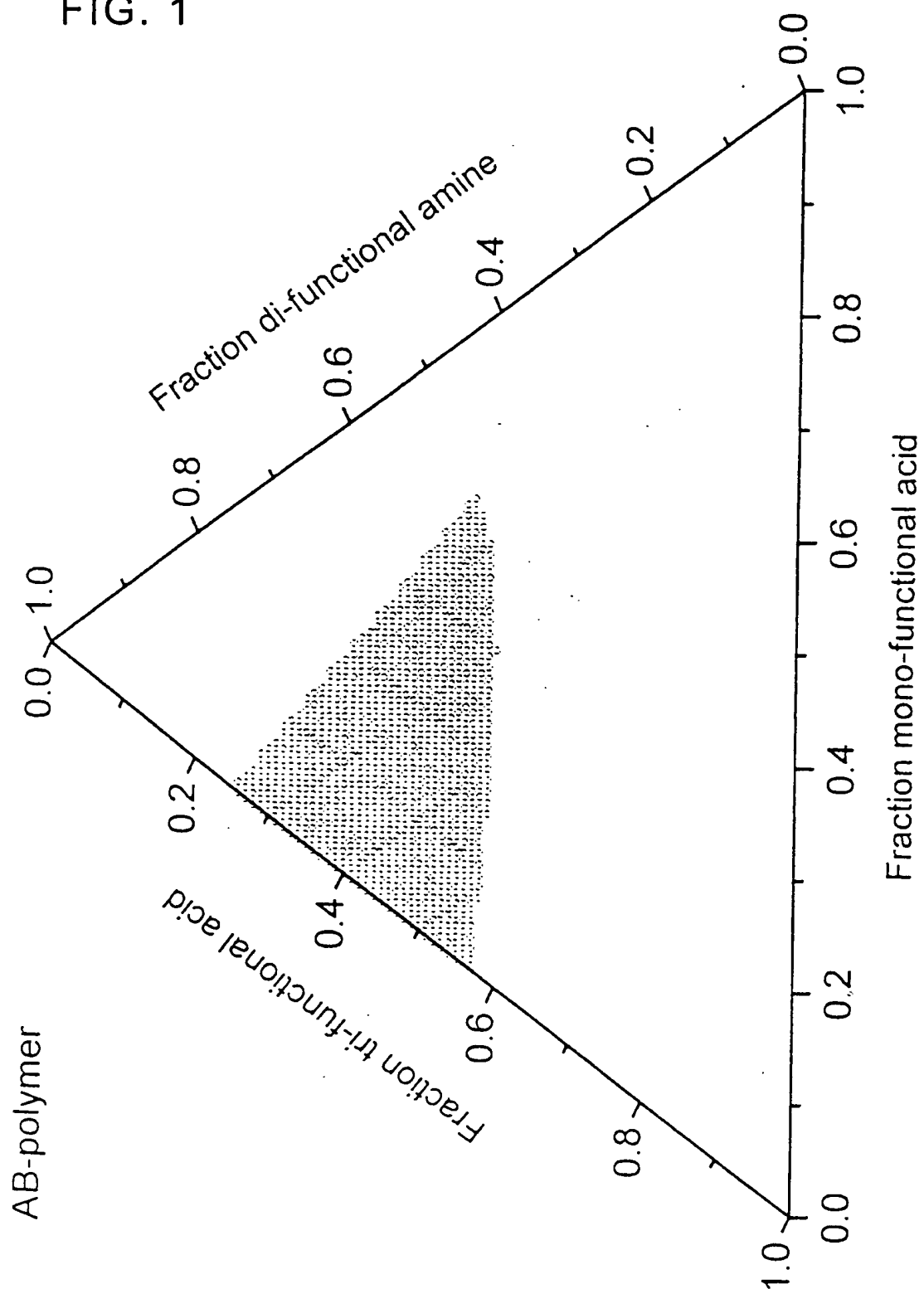


FIG. 2

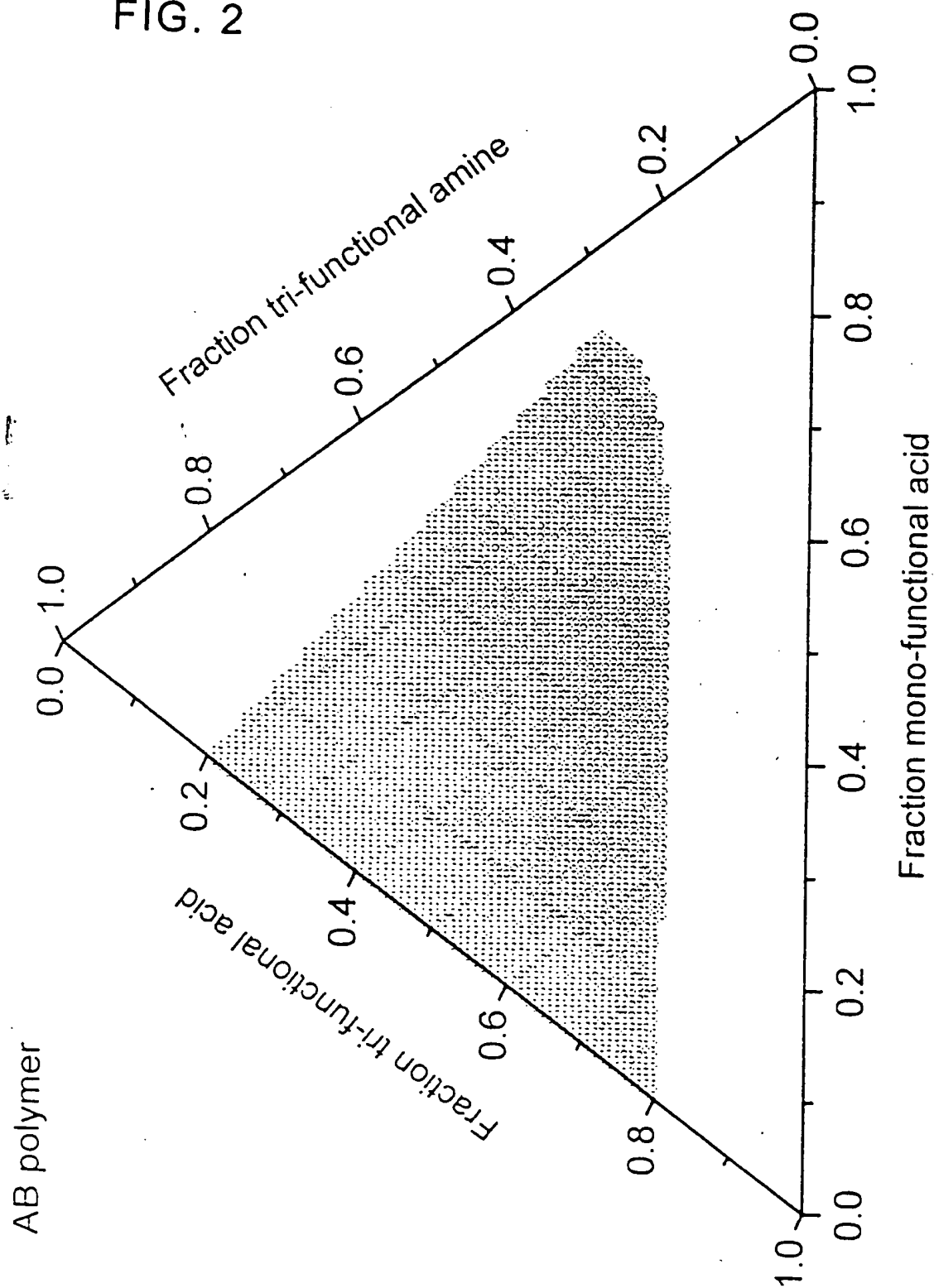


FIG. 3

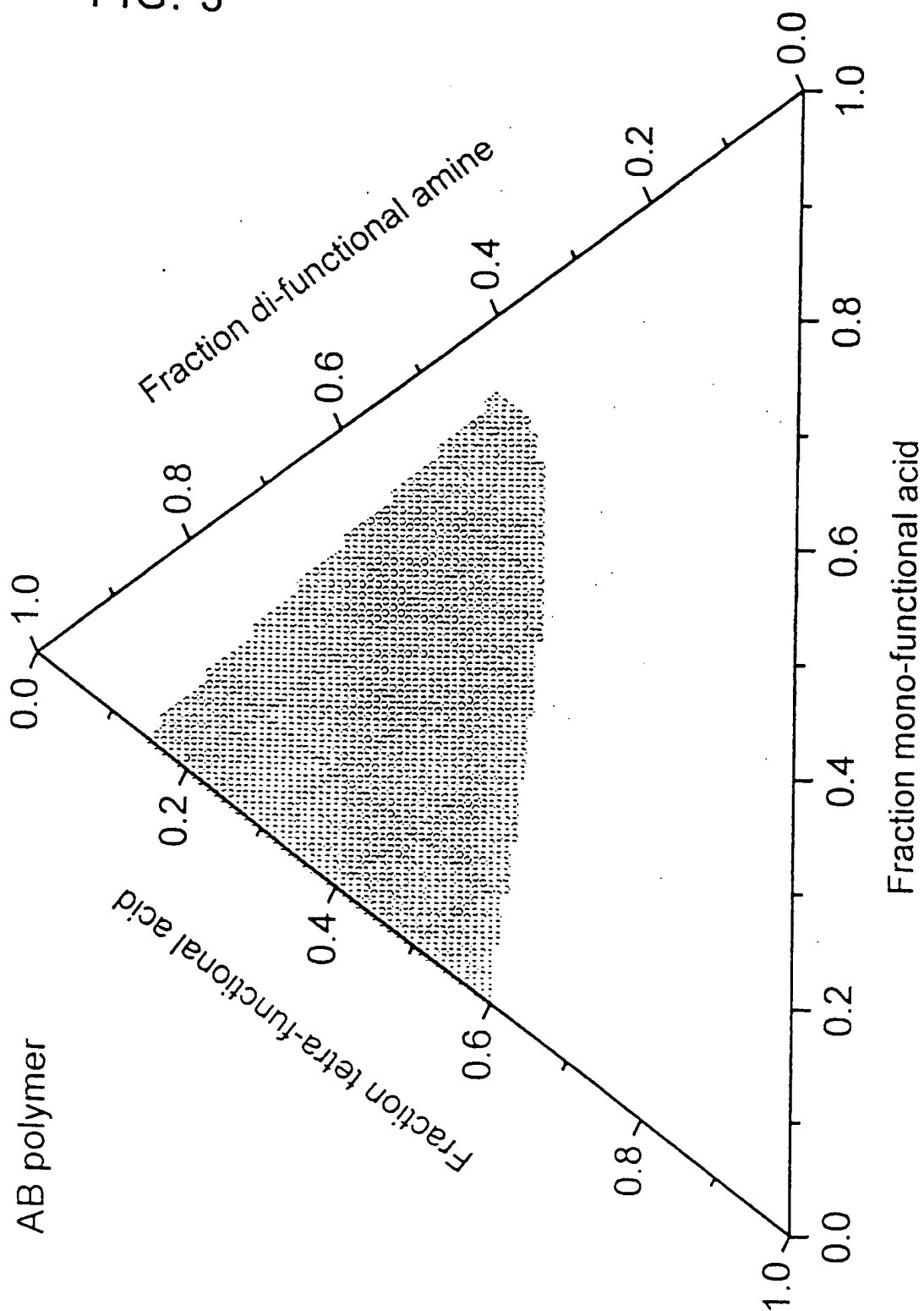


FIG. 4

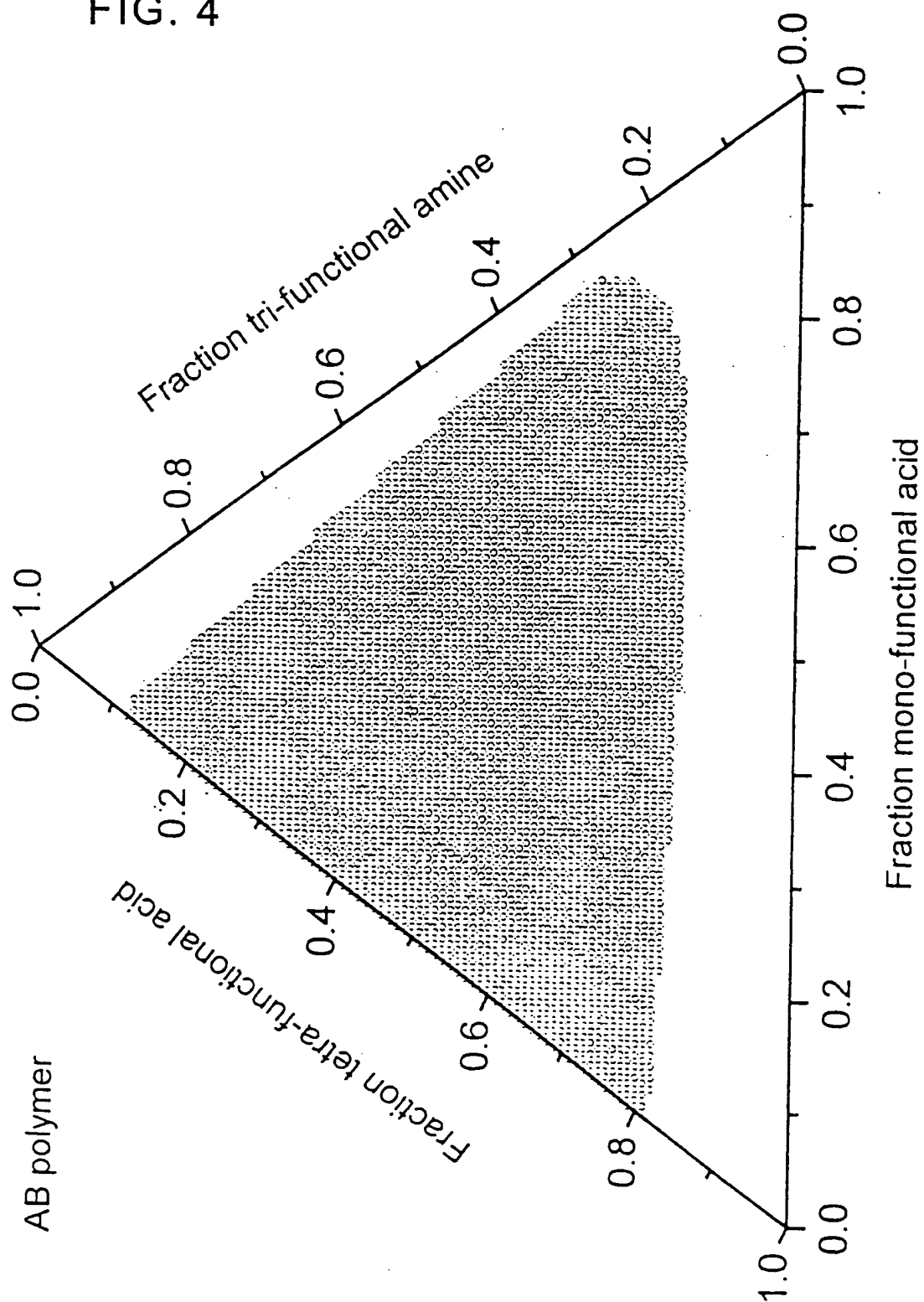


FIG. 5

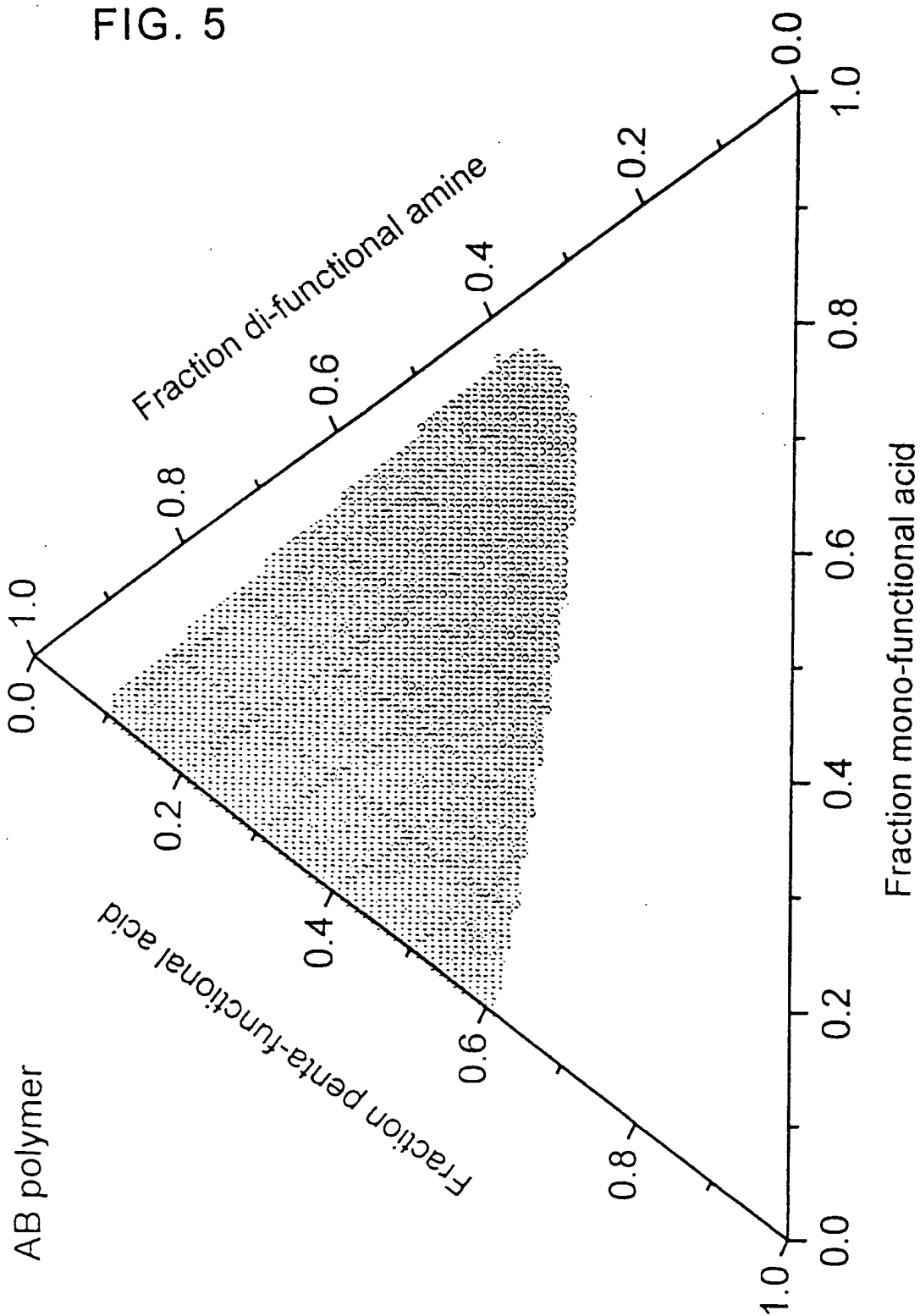


FIG. 6

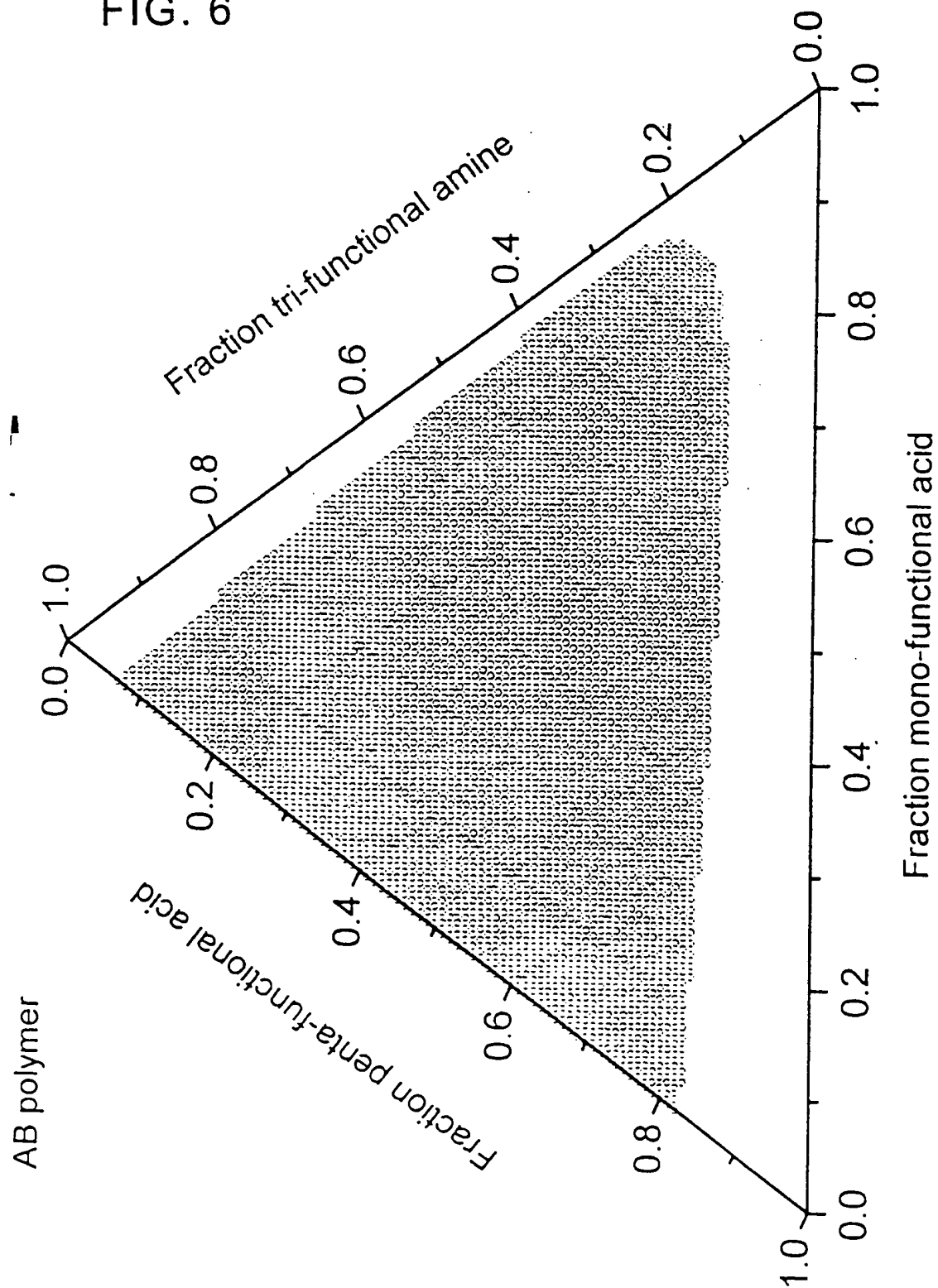


FIG. 7

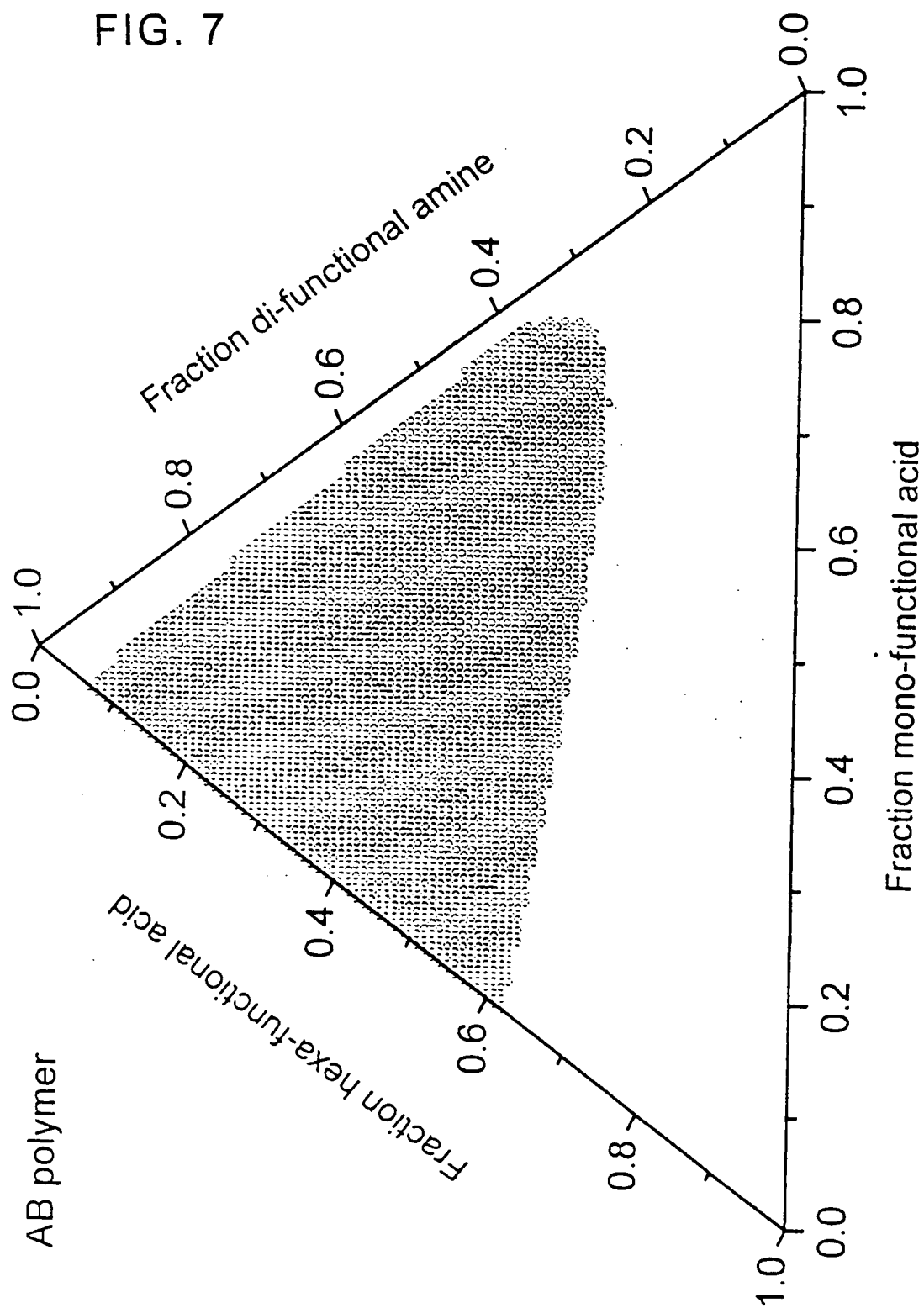
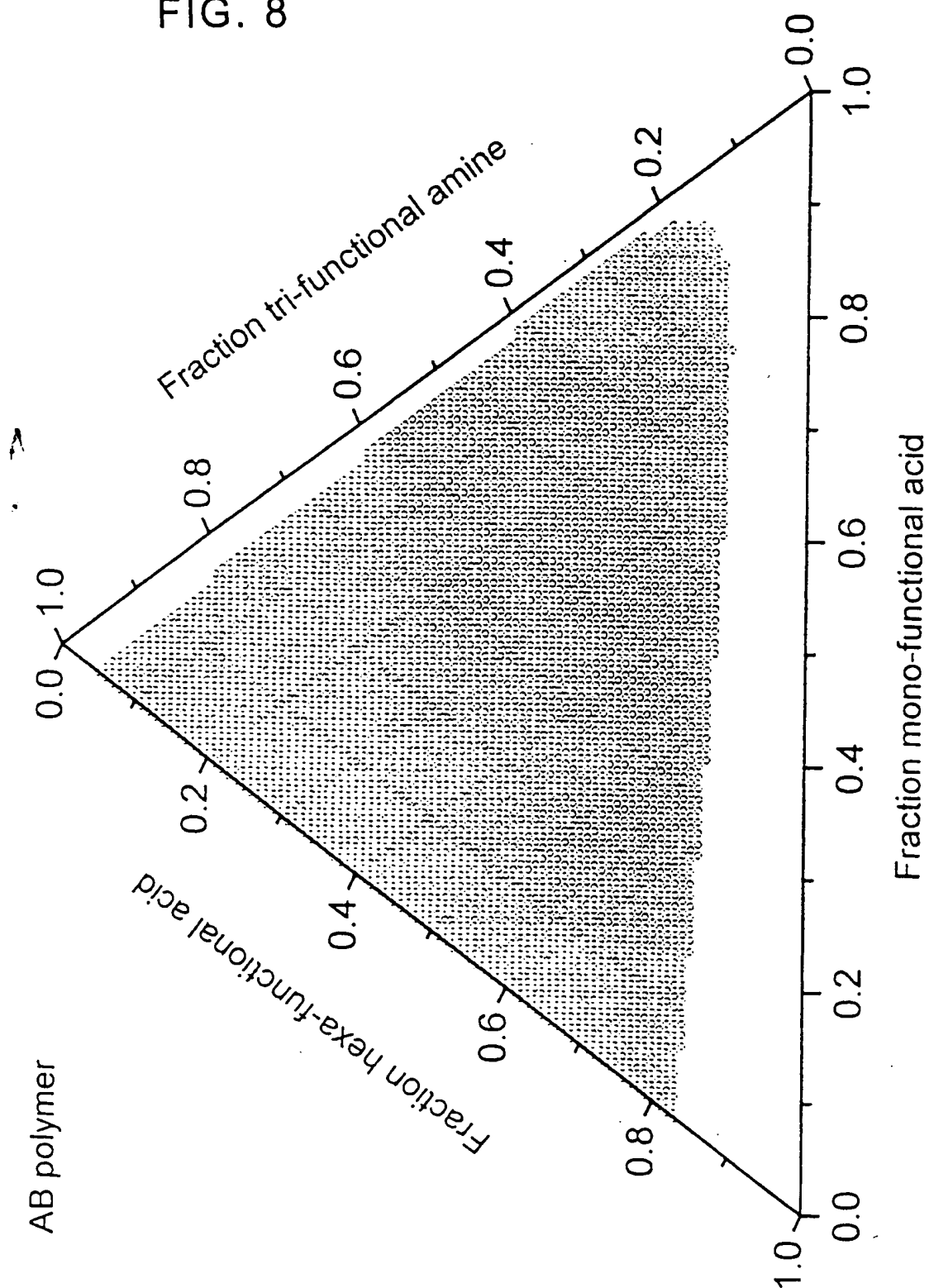
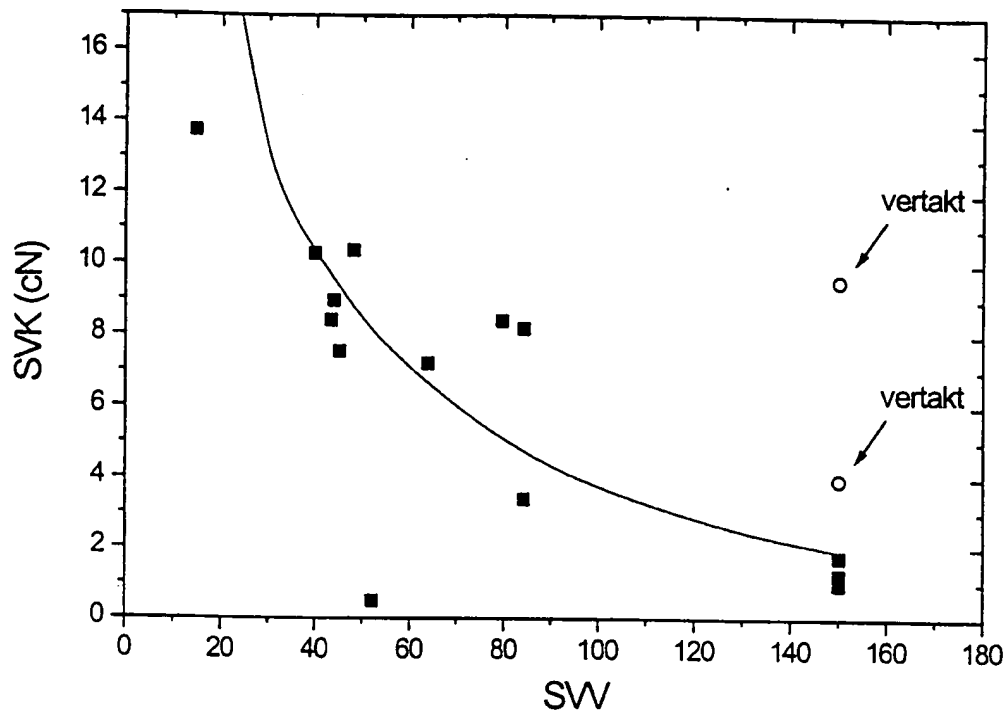


FIG. 8





■ : linear polyamide ; ○ : branched polyamide according
5 to the invention.

SVK : melt drawing force

SVV : melt drawing degree

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/ /00764

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G69/48 C08G69/08 C08G69/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 345 648 A (INVENTA AG) 13 December 1989 (1989-12-13) cited in the application	
A	WO 97 24388 A (NYLTECH ITALIA ;SNIARICERCHE (IT); CUCINELLA ANTONINO (IT); SILVES) 10 July 1997 (1997-07-10)	
A	EP 0 149 986 A (MONSANTO CO) 31 July 1985 (1985-07-31)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

3 April 2000

Date of mailing of the international search report

12/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 851 epo nl,
Fax (+31-70) 340-3018

Authorized officer

Leroy, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interns / Application No

PCT/ 9/00764

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0345648 A	13-12-1989	DE 3917927 A	14-12-1989
		DE 58909415 D	12-10-1995
		ES 2076172 T	01-11-1995
		JP 2064128 A	05-03-1990
WO 9724388 A	10-07-1997	FR 2743077 A	04-07-1997
		IT MI952779 A	30-06-1997
		AU 1379297 A	28-07-1997
		BR 9612358 A	13-07-1999
		EP 0869987 A	14-10-1998
		PL 327578 A	21-12-1998
EP 0149986 A	31-07-1985	US 4617355 A	14-10-1986
		AT 33141 T	15-04-1988
		AU 564746 B	27-08-1987
		AU 3650184 A	20-06-1985
		BR 8406335 A	08-10-1985
		CA 1225179 A	04-08-1987
		DD 233850 A	12-03-1986
		DK 591284 A	13-06-1985
		ES 538458 D	01-11-1987
		ES 8800299 A	01-01-1988
		ES 551530 D	16-10-1987
		ES 8800295 A	01-01-1988
		JP 1696191 C	28-09-1992
		JP 3063973 B	03-10-1991
		JP 60168724 A	02-09-1985
		KR 8802312 B	22-10-1988
		PT 79654 A, B	01-01-1985
		ZA 8409641 A	30-10-1986
		CS 8409620 A	17-09-1987

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☒ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☒ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.